PTO 07-[0895]

Korean Patent

2001-0037483

POLYESTER FILM FOR LAMINATING IN WHICH A PRIMER LAYER IS FORMED AND METHOD OF MANUFACTURE THEREOF

[Praimokungi Hyeongsongdoin Lamineitingyong Poriester Film Mip Ku Jeizo Bangbeop]

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UNITED STATES PATENT AND TRADEMARK OFFICE

Washington, D.C. November 2006

Translated by: Schreiber Translations, Inc.

Country	:	Korea
Document No.	:	2000-0037483
Document Type	:	Laid-Open
Language	:	Korean
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Applicant	:	SKC Co., Ltd.
IPC	:	B 32 B 27/36
Application Date	:	October 18, 1999
Publication Date	:	May 7, 2001
Foreign Language Title	:	Praimokungi Hyeongsongdoin Lamineitingyong Poriester Film Mip Ku Jeizo Bangbeop
English Title	:	POLYESTER FILM FOR LAMINATING IN WHICH A PRIMER LAYER IS FORMED AND METHOD OF MANUFACTURE THEREOF

/1[1]

Specification

1. Title of the invention

Crystal Growth Apparatus

2. Detailed explanation of the invention

(Purpose of the invention)

(Technical field of the invention and prior art of the field)

The present invention pertains to a polyester film for laminating. More specifically, the present invention pertains to a biaxially oriented polyester film for laminating in which the adhesive strength is improved by inline-coating a primer composition and its manufacturing method.

Also, the present invention pertains to a safety glass on which the above-mentioned biaxially oriented polyester film for laminating is laminated.

The inline coating being used in the present invention means that coating is carried out before a thermal fixing stage among the manufacturing processes of a polyester film is /2 applied, and the offline coating means that coating is carried out after the manufacture of a polyester film is completed.

[1] Numbers in the margin indicate pagination in the foreign text.

In general, since oriented polymeric films, especially biaxially oriented polyester films such as polyethylene terephthalate (PET) have high transparency and excellent mechanical properties, they are frequently used in the field of wrapping materials, magnetic tapes, graphic films, protective films, etc., and the polyester films are applied as materials for regulating the transparency of substances such as glass. In particular, they are used as protective layers of automobile glass products such as sunroof panels and rear windows of automobiles.

Generally, the above-mentioned glass product consists of a glass sheet, a high-strength film such as polyester, and a sheet composed of polyvinyl butyral for forming an interfacial adhesive layer between the glass and the high-strength film. The sheet composed of polyvinyl butyral existing between the glass sheet and the polyester film has a function of preventing the breakdown of the glass when an automobile accident is caused, and the polyester film plays a role of reducing the human body damage by suppressing the rupture of broken glass pieces.

The technique and structure in which the polyester film is applied to an automobile glass surface is registered in U.S. Patent No. 4,973,364, however though the sheet composed of

polyvinyl butyral used as an adhesive layer between the glass sheet and the polyester film has excellent adhesive strength, the adhesive strength with the polyester film is insufficient at a temperature of the freezing point or lower of water (hereinafter, the temperature at the freezing point or lower means a temperature of the freezing point or lower of water).

As countermeasures to solve this problem, a method that improves the adhesive strength between the sheet composed of polyvinyl butyral and the polyester by utilizing a corona discharge or a flaming treatment as shown in U.S. Patent No. 3,900,673, a method that improves the adhesive strength with the sheet composed of polyvinyl butyral by spreading gelatin, polyvinylidene chloride or acryl latex on the polyester film, etc., can be mentioned. However, even in case these methods are used, the adhesive strength of the polyester film and the sheet composed of polyvinyl butyral is still insufficient at a temperature of the freezing point or lower.

Various primer coating techniques for imparting the adhesive strength of the polyester film and other substances have been continuously developed up to now. For example, there are a method that coats polyvinylidene chloride in U.S. Patent No. 2,698,240, a method that coats a thermosetting acryl or methacryl in U.S. Patent No. 3,819,773, a method that coats a

water-dispersible copolymerized polyester on a polyester film and used as an adhesive layer in laminating with a nylon film in U.S. Patent Nos. 3,563,942 and 3,779,993, a method that spreads a solvent type polyurethane and applies it as an adhesive layer, etc. However, they are subjected to the restrictions in the production due to the environmental regulation problems in actuality.

Recently, in U.S. Patent No. 4,663,228 using a silane coupling agent, the adhesive strength with an ionomer resin has been rendered by spreading N-2-aminoethyl-3-aminopropyltrimethoxy silane (trade name: Z-6020, Down Corning) on a polyester film.

However, in all of the above-mentioned methods, there is a delamination problem due to the absence of the adhesive strength of the sheet composed of polyvinyl butyral and the polyester film at a temperature of the freezing point or lower.

(Technical problems to be solved by the invention)

Therefore, the technical purpose of the present invention is to provide a biaxially oriented polyester film for laminating in which the adhesive strength is improved to the degree that no delamination is caused at a temperature of the freezing point or lower.

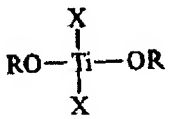
Another technical purpose of the present invention is to provide a method for manufacturing the above-mentioned film.

Also, another technical purpose of the present invention is to provide a safety glass on which the above-mentioned polyester film is laminated.

(Constitution and operation of the invention)

In order to achieve the above-mentioned technical purpose, the present invention provides a biaxially oriented polyester film for laminating in which a composition composed of 0.1-10.0 wt% water-soluble titanium chelate compound represented by the following chemical formula 1 and the balance water is spread on one surface or both surfaces, so that a primer layer is formed. /3

(Chemical formula 1)



In the above-mentioned formula, R represents an alkyl group having 1-8 carbons, and X represents a chelating substance.

In the present invention, it is preferable for the above-mentioned composition to further include 0.1-0.5 wt% weak acid to accelerate the hydrolysis of the titanate chelate compound.

In the present invention, the above-mentioned weak acid is preferably acetic acid or phosphoric acid.

In the present invention, the above-mentioned water-soluble titanium chelate compound is preferably one kind being selected from a group comprised of titanium acetyl acetate, titanium ethyl acetoacetate, and triethanol amine titanate, and triethanol amine titanate is more preferable.

In the present invention, the above-mentioned primer layer is preferably formed so that the water-soluble titanium chelate compound may be included at a solid fraction of 0.001-0.1 g/m^2.

In order to achieve the above-mentioned other technical purpose, the present invention provides a method for manufacturing a biaxially oriented polyester film for laminating characterized by including (a) a step that spreads a composition composed of 0.1-10.0 wt% water-soluble titanium chelate compound represented by the above-mentioned chemical formula 1 on one surface or both surfaces of an amorphous polyester sheet and the balance water; and (b) a step that thermally fixes an amorphous sheet on which the above-mentioned composition is spread.

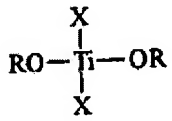
In the present invention, the above-mentioned composition spreading step can be applied before stretching the above-mentioned amorphous sheet in the vertical direction, before stretching the sheet in the horizontal direction after stretching it in the vertical direction, or before the thermal fixing step after stretching the sheet in the horizontal direction.

In order to achieve the above-mentioned other technical purpose, as mentioned above in detail, the present invention provides a polyester film complex glass sheet characterized by including a biaxially oriented polyester film for laminating in which a primer layer is formed; a first sheet(s) composed of polyvinyl butyral being laminated on the surface on which the primer layer of the biaxially oriented polyester film has been formed; and a second sheet(s) composed of glass being laminated on the above-mentioned first sheet.

The present invention has been completed by finding out that the adhesive strength of a polyester film can be improved by a primer layer composed of a hydrolyzed water-soluble titanium chelate compound. First, the composition for forming the above-mentioned primer layer is explained.

The above-mentioned primer composition is composed of 0.1-10.0 wt% water-soluble titanium chelate represented by the following chemical formula 1 and the balance water.

(Chemical formula 1)



In the above-mentioned formula, R represents an alkyl group /4 having 1-8 carbons, and X represents a chelating substance.

In the above-mentioned R, a hydroxyl group as a hydrophilic group being hydrolyzed like the above-mentioned reaction equation 1 is introduced, and the above-mentioned chelating substance X promotes the adhesive strength between the polymeric films by an exchange reaction and an addition reaction with other polymeric substances such as hydroxyl group or carboxyl group like the following reaction equation 2.

$Ti(X)_2(OR)_2$ + polymer (including an unsaturated group/double bond, hydroxyl group, carboxyl group, etc.) -> $Ti(O\text{-polymer})_2(OR)_2 + 2XH$

In the above-mentioned reaction equations 1 and 2, R represents an alkyl group having 1-8 carbons, and X represents a chelating substance.

The above-mentioned water-soluble titanium chelate compound is not specially limited as long as the above-mentioned chelating substance X can carry out the exchange reaction and the addition reaction with the surface functional group of other polymers, however it is preferably one kind being selected from a group comprised of titanium acetyl acetate (TAA), titanium ethyl acetoacetate (TEA), and triethanol amine titanate (TEAT). Triethanol amine titanate is more preferable.

Also, the above-mentioned primer composition can further include 0.1-0.5 wt% weak acid to accelerate the hydrolysis of the water-soluble titanate chelate compound, and the above-mentioned weak acid is preferably acetic acid or phosphoric acid.

Next, the biaxially oriented polyester film for laminating and its manufacturing method of the present invention are explained.

The biaxially oriented polyester film for laminating of the present invention is a film in which the above-mentioned primer composition is spread on one surface or both surfaces and the primer layer is formed, and the above-mentioned primer layer is preferably formed so that the water-soluble titanium chelate compound may be included at a solid fraction of 0.001-0.1 g/m^2.

The primer composition in the present invention can be used alone, however a thermosetting acryl or methacryl polymer used in U.S. Patent No. 4,214,035 can also be used in combination. In other words, in case the primer composition of the present invention is coated on one surface, a thermosetting acryl or methacryl polymer can be spread on its opposite surface.

Also, in the present invention, a small amount of colloidal silica, pH regulator, weighting agent, etc., can be added to the primer composition in the range where the properties of the titanium chelate are not hindered.

Next, the method for manufacturing the biaxially oriented polyester film for laminating of the present invention is explained.

First, a polyester chip is manufactured by the condensation reaction of a glycol component and a dicarboxylic acid component, and an amorphous sheet is formed by melt-extracting the above-mentioned chip. The step form manufacturing the amorphous sheet is based on an ordinary method well known in the technical field of the present invention.

Though there is no particular limitation in the glycol component and the dicarboxylic acid component usable in the present invention, for example, ethylene glycol or butanediol can be mentioned as the glycol component, and as the

dicarboxylic acid component, terephthalic acid, isophthalic acid, or sebacic acid can be mentioned.

Next, the above-mentioned primer component is spread on the above-mentioned amorphous sheet, and this spreading step can be carried out at an optional step prior to a thermal fixing step among the manufacturing processes of the polyester film. In other words, a spreading method prior to the vertical stretching process as shown in British No. Patent No. 141,564 and a spreading method between a vertical stretch and a horizontal stretch and a spreading method prior to a thermal fixing as shown in U.S. Patent No. 4,214,035 can be mentioned.

Then, as the method for spreading the primer composition, a general method known in the technical field of the present invention such as a spreading method using a gravure roll or reverse gravure roll, a spreading method using a mayer bar, and a spreading method using an air knife.

Also, the conditions of the stretch step are not particularly limited as long as they are well known in the technical field of the present invention, and for example, a polyester film can be manufactured by stretching the amorphous sheet 3-5 times in the horizontal direction after stretching it 3-5 times in the vertical direction.

The primer composition spread as mentioned above is /5 thermally set and dried in a thermal fixing section in which 210-240°C is maintained and coated on the polyester film, so that the biaxially oriented polyester film for laminating of the present invention is completed. Even if the waste film being generated in the above-mentioned manufacturing processes is mixed and processed in the manufacturing processes of a pure polyester film, the regenerated film is neither lowered in the physical properties nor discolored.

Next, the polyester composite glass sheet and its manufacturing method of the present invention are explained.

The polyester film complex glass sheet of the present invention has a structure including a biaxially oriented polyester film for laminating in which a primer layer composed of a water-soluble titanium chelate, wherein the above-mentioned primer composition is spread and hydrolyzed, is formed on one surface or both surfaces; a first sheet composed of polyvinyl butyral being laminated on the surface on which the primer layer of the above-mentioned biaxially oriented polyester film has been formed; and a second sheet composed of glass being laminated on the above-mentioned first sheet.

The above-mentioned polyester film composite glass sheet can be manufactured by laminating at a temperature of 125-225°C

and a pressure of 150-300 psi after laminating a sheet composed of polyvinyl butyral being generally used in a glass processing field on the surface, on which the primer layer of the biaxially oriented polyester film manufactured as mentioned above has been formed, and laminating a sheet composed of glass on it.

In the above-mentioned polyester film composite glass sheet, if the primer layer is formed on both surfaces, sheets composed of polyvinyl butyral are laminated on both surfaces, and sheets composed of glass are laminated on it, so that the composite glass sheet can be manufactured. At that time, the laminating temperature and pressure are the same as those mentioned above.

Next, the biaxially oriented polyester film for laminating and the polyester film composite glass sheet of the present invention are explained in detail through application examples and comparative examples. However, it is apparent that the following application examples are only the illustrations for explaining the present invention.

Application Example 1

1.0 wt% triethanol amine titanate (TEAT) was dispersed into water, and 0.2 wt% acetic acid was added to it, so that a hydrolyzed primer composition was prepared.

Next, dimethyl terephthalate and ethylene glycol were mixed at an equivalent ratio of 1:2, and a bishydroxyethylene terephthalate (BHET) was generated by putting an ordinary transesterification catalyst. Then, antimony trioxide as a polycondensation catalyst was put at 0.03 wt% based on the weight of the dimethyl terephthalate, and the polycondensation reaction was completed, so that a PET chip was manufactured.

An amorphous sheet was prepared by melt-extracting the above-mentioned chip, and the above-mentioned composition prepared was spread on one surface of a polyester film in which the amorphous sheet was stretched 3.5 times at 80°C in the vertical direction by a mayer bar coating method, stretched 3.5 times at 230°C in the horizontal direction, and dried, so that a polyester film with a thickness of 50 μm on which the water-soluble composition solution was spread was manufactured.

Application Example 2

Using the same apparatus and method as those of Application Example 1, a polyester film on which a primer composition in which the concentration of triethanol amine titanate (TEAT) was set to 2.0 wt% was spread was manufactured.

Application Example 3

Using the same apparatus and method as those of Application Example 1, a polyester film on which a primer composition,

wherein 1.0 wt% titanium acetyl acetate (TAA) was dispersed into water, was spread was manufactured.

Application Example 4

Using the same apparatus and method as those of Application Example 1, a polyester film on which a primer composition, wherein 1.0 wt% titanium ethyl acetoacetate (TEA) was dispersed into water, was spread was manufactured.

Comparative Example 1

Using the same apparatus and method as those of Application Example 1, a polyester film on which a primer composition, wherein 4.0 wt% acryl latex was dispersed into water, was spread was manufactured as shown in U.S. Patent No. 4,571,363.

Comparative Example 2

Using the same apparatus and method as those of Application Example 1, a polyester film on which a primer composition, wherein 4.0 wt% water-soluble copolyester resin was dispersed into water, was spread was manufactured as shown in U.S. Patent No. 4,493,872.

Comparative Example 3

Using the same primer composition as that of Application Example 1, a polyester film on which the above-mentioned composition was spread offline under the conditions of a line speed of 40 m/min, a dryer temperature of 150°C, and a gravure

cylinder (150 quad) on a polyester film with a thickness of 50 m was manufactured.

Comparative Example 4

Using the same apparatus and method as those of Comparative Example 3, a polyester film on which a primer composition, wherein the concentration of triethanol amine titanate was set to 2.0 wt%, was spread offline was manufactured.

<Adhesive strength evaluation method> In order to evaluate the/6 adhesive strength of the polyester films manufactured in the above-mentioned application examples and comparative examples and a sheet composed of polyvinyl butyral, a sheet composed of polyvinyl butyral (trade name: Saflex RA, maker: Monsanto Chemical Company) being used in an automobile safety glass was put on the surface on which the primer layer of the polyester film cut into a size of 100 mm x 30 mm, and a glass sheet was superposed on it. Then, strawboards were respectively supported to the top and bottom of the above-mentioned structures to make the temperature and the pressure uniform when laminating.

The above final structures were laminated at a temperature of 150°C and a pressure of 150 psi for 30 min, cooled to normal temperature, and cut into a width of 1 inch by a medical scalpel, so that samples for a peeling test were prepared.

As for the peeling adhesive strength of the above-mentioned structures, a T type delamination was measured five times at a speed of 200 mm/min under the conditions of normal temperature (23°C) and the freezing temperature or lower (-10°C) by using an UTM of Instrong Co., and its average value was calculated. The results were shown in Table I.

(Table I)

	코팅방식	코팅물질	코팅량(중량%)	접착 강도(Kg/inch)	
				23°C	-10°C
실시예 1	인라인	TEAT	1.0	6.8	3.6
실시예 2	인라인	TEAT	2.0	7.5	4.5
실시예 3	인라인	TAA	1.0	4.0	0.4
실시예 4	인라인	TEA	1.0	3.8	0.3
비교예 1	인라인	아크릴라텍스	4.0	1.7	0.0
비교예 2	인라인	코폴리에스테르	4.0	0.0	0.0
비교예 3	오프라인	TEAT	1.0	1.6	0.0
비교예 4	오프라인	TEAT	2.0	2.0	0.0

1. Coating method
2. Coating substance
3. Amount coated (wt%)
4. Peel strength (kg/inch)
5. Application Example 1
6. Application Example 2
7. Application Example 3
8. Application Example 4
9. Comparative Example 1
10. Comparative Example 2

11. Comparative Example 3

12. Comparative Example 4

13. Inline

14. Offline

15. Acryl latex

16. Copolyester

As shown in the above-mentioned Table I, in the polyester films of Application Examples 1 and 2 on which the TEAT were spread, it can be confirmed that the peeling adhesive strength was more excellent than that of the polyester films on which other primers were coated at normal temperature or a temperature of the freezing temperature or lower.

On the other hand, in the polyester films of Application Examples 3 and 4 on which the TAA and the TEA were respectively spread, the peeling adhesive strength at normal temperature was excellent, and compared with Application Examples 1 and 2 using the TEAT at a temperature of the freezing point or lower, though the peeling adhesive strength was more or less inferior, the

peeling adhesive strength was better than that of the comparative examples.

Also, in the polyester films of Comparative Examples 1 and 2 on which the acryl latex and the water-soluble copolyester were respectively spread, it was confirmed that the peeling adhesive strength at a temperature of the freezing point or lower was not exerted.

Then, even in the same composition, it could be confirmed that the adhesive strength of the polyester film spread inline according to the spreading method and the polyvinyl butyral was much more excellent than that of the polyester film spread offline.

(Effects of the invention)

As mentioned above, in the biaxially oriented polyester film for laminating of the present invention, the adhesive strength with the sheet composed of polyvinyl butyral, compared with the conventional polyester film, is excellent at a temperature of the freezing temperature or lower as well as normal temperature.

Also, unlike the existing primer composition using an organic solvent, the composition being used in the present invention uses water as a solvent, so that the environmental

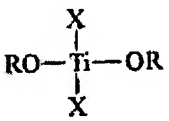
pollution and the fire risk are little and the production cost is low.

The present invention has been explained by the application examples for reference, however they are only the illustrations. Any person with ordinary skill in the technical field pertaining to the present invention understands that the present invention can be variously modified and uniformly applied. Therefore, the true technical protective range of the present invention should be determined according to the technical concept of the attached patent claim scope.

3. Claims /7

1. A biaxially oriented polyester film for laminating, characterized by the fact that a composition composed of 0.1-10.0 wt% water-soluble titanium chelate compound represented by the following chemical formula 1 and the balance water is spread on one surface or both surfaces, so that a primer layer is formed.

(Chemical formula 1)



In the above-mentioned formula, R represents an alkyl group having 1-8 carbons, and X represents a chelating substance.

2. The biaxially oriented polyester film for laminating of Claim 1, characterized by the fact that the above-mentioned composition further includes 0.1-0.5 wt% weak acid to accelerate the hydrolysis of the titanate chelate compound.

3. The biaxially oriented polyester film for laminating of Claim 2, characterized by the fact that the above-mentioned weak acid is acetic acid or phosphoric acid.

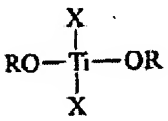
4. The biaxially oriented polyester film for laminating of Claim 1, characterized by the fact that the above-mentioned water-soluble titanium chelate compound is one kind being selected from a group comprised of titanium acetyl acetate, titanium ethyl acetoacetate, and triethanol amine titanate.

5. The biaxially oriented polyester film for laminating of Claim 4, characterized by the fact that the above-mentioned water-soluble titanium chelate compound is triethanol amine titanate.

6. The biaxially oriented polyester film for laminating of Claim 1, characterized by the fact that the above-mentioned primer layer is formed so that the water-soluble titanium chelate compound may be included at a solid fraction of 0.001-0.1 g/m^2.

7. A method for manufacturing a biaxially oriented polyester film for laminating, characterized by including (a) a step that spreads a composition composed of 0.1-10.0 wt% water-soluble titanium chelate compound represented by the above-mentioned chemical formula 1 on one surface or both surfaces of an amorphous polyester sheet and the balance water; and (b) a step that thermally fixes an amorphous sheet on which the above-mentioned composition is spread.

(Chemical formula 1)



In the above-mentioned formula, R represents an alkyl group /8 having 1-8 carbons, and X represents a chelating substance.

8. The method for manufacturing a biaxially oriented polyester film for laminating of Claim 7, characterized by the fact that the above-mentioned composition spreading step is applied before stretching the above-mentioned amorphous sheet in the vertical direction.

9. The method for manufacturing a biaxially oriented

polyester film for laminating of Claim 7, characterized by the fact that the above-mentioned composition spreading step is applied before stretching the above-mentioned amorphous sheet in the horizontal direction after stretching the sheet in the vertical direction.

10. The method for manufacturing a biaxially oriented polyester film for laminating of Claim 7, characterized by the fact that above-mentioned composition spreading step is applied before the thermal fixing step after stretching the above-mentioned amorphous sheet in the horizontal direction.

11. A polyester film complex glass sheet, characterized by including the biaxially oriented polyester film for laminating of Claim 1; a first sheet(s) composed of polyvinyl butyral being laminated on the surface on which the primer layer of the above-mentioned biaxially oriented polyester film has been formed; and a second sheet(s) composed of glass being laminated on the above-mentioned first sheet.